

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ^S : C07C 41/01	A1	(11) International Publication Number: WO 93/16976 (43) International Publication Date: 2 September 1993 (02.09.93)
(21) International Application Number: PCT/US93/01850 (22) International Filing Date: 17 February 1993 (17.02.93) (30) Priority data: 07/838,645 20 February 1992 (20.02.92) US 08/001,954 8 January 1993 (08.01.93) US (71) Applicant: EXXON RESEARCH AND ENGINEERING COMPANY [US/US]; 180 Park Avenue, P.O. Box 390, Florham Park, NJ 07932-0390 (US). (72) Inventors: SISKIN, Michael ; 105 Lindsley Drive, Morristown, NJ 07960 (US). SALEH, Ramzi, Yanni ; 13 Fir Court, Flemington, NJ 08822 (US). KNUDSEN, George, Andrew ; 1932 Mary Ellen Lane, Scotch Plains, NJ 07076 (US).		(74) Agents: SCUORZO, Linda, M. et al.; Exxon Research and Engineering Company, P.O. Box 390, Florham Park, NJ 07932-0390 (US). (81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: PROCESS FOR RECYCLING POLYMERS HAVING REPEATING ETHER LINKAGES (57) Abstract The present invention is a process for converting high molecular weight essentially water insoluble polymers having repeating or multiple ether linkages in the polymer backbone into their corresponding alcohols and other monomeric and lower weight oligomeric units by forming an aqueous mixture of the polymer in a ratio by weight of liquid water to polymer of at least 1:1, preferably neutral water, and heating the mixture under autogeneous pressure at a temperature of from about 200 °C to about the critical temperature of water (374 °C), more preferably from about 200 °C up to about 350 °C. Heating is continued for a period of time sufficient to depolymerize the polymer, depending on temperature and the amount of water present, and the number of polymeric ether linkages in the feedstock, and the amount of conversion desired.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Cote d'Ivoire	LJ	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

- 1 -

PROCESS FOR RECYCLING POLYMERS HAVING REPEATING ETHER LINKAGES

This is a Continuation-in-Part application of U.S. Serial No. 838,645 filed February 20, 1992.

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to a process for converting polymers having multiple or repeating ether linkages in the backbone to alcohols, and other monomeric and lower molecular weight oligomeric units by heating with liquid water.

Description of Related Art

Generally speaking, waste polymers containing repeating ether linkages are less commercially valuable than the corresponding alcohol and monomeric and lower molecular weight oligomeric products which may be produced by cleavage of (C-O) linkages in the polymer backbone. Such waste polymers are generally not easily biodegradable and due to their high molecular weight also are not water soluble. Current processes, such as described in U.S. Patent 4,608,658, require the addition of catalysts to depolymerize these polymers. The process of the present invention has advantages in that it may be practiced without the addition of a catalyst in an environment that requires only the polymer and water as starting materials, and that it degrades the C-O bond in the (ether) linkages in the polymer backbone.

SUMMARY OF THE INVENTION

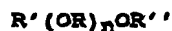
The present invention is a simplified process for depolymerizing water insoluble high molecular weight polymers having a backbone of multiple or repeating ether linkages. These polymers have molecular weights that are sufficiently great to render the starting polymer essentially not soluble in water at 25°C. Typically, the molecular weight of such polymers is greater than about 5,000. The

- 2 -

process converts these polymers into their corresponding lower molecular weight products, that is: alcohols, monomeric products, and lower molecular weight oligomeric products. It comprises forming an aqueous mixture of a water insoluble high molecular weight polymer having multiple or repeating ether linkages in the backbone and sufficient liquid water, preferably water having a pH of from about 7 to about 3.5, more preferably neutral water, pH of about 7.0 at room temperature, and heating the mixture under autogeneous pressure at a temperature of from about 200°C up to the critical temperature of water which is about 374°C, preferably from about 200°C to about 350°C. Heating is continued for a period of time sufficient to depolymerize the polymer.

DETAILED DESCRIPTION OF THE INVENTION

The invention is applicable to the cleavage of high molecular weight polymers having multiple or repeating ether linkages in the backbone. Polymers acceptable as starting materials are any high molecular weight polymers having repeating or multiple ether linkages in the polymer backbone. Such polymers are typically not water soluble and generally have an average molecular weight of greater than or equal to about 5,000, more typically from about 20,000 and most typically from about 100,000. The polymer has the formula:



wherein n is a whole number typically equal to or greater than 100, depending on the molecular weight of the polymer and wherein R, R' and R'' each is selected from the group consisting of hydrocarbon groups and substituted hydrocarbon groups, wherein the hydrocarbon group and substituted hydrocarbon group may be aliphatic (including linear, branched and cyclic aliphatic), aromatic and mixtures thereof. If aromatic hydrocarbons are present as part of the ether backbone, aromatic hydrocarbons having at least two aromatic rings (e.g., naphthalene) are preferred to be the ether linkage in the polymer chain, rather than only one ring aromatics (e.g., naphthyl-O-phenyl, or naphthyl-O-naphthyl, etc. is preferred over phenyl-phenyl) as

- 3 -

unsubstituted phenyl-O-phenyl bonds are not degraded easily at reaction conditions, except if one of the phenyl rings is (a) replaced by a higher aromatic ring, (b) replaced by an aliphatic group, or (c) substituted with, e.g., a hydroxyl, amino, alkoxy, etc. group, the ether bond to that ring may be degraded in the process of the present invention. Further, R, R' and R'' may be the same or different, provided that R, R' and R'' are not all unsubstituted phenyl groups; i.e., selected from the group consisting of aliphatic and higher aromatic hydrocarbon groups and mixtures thereof. Thus, the polymer may be any known polymer having repeating or multiple ether linkages in the backbone, such as linear, block, radial or random polymers (including copolymers). Included in random polymers are those wherein R, R' and R'' are distributed randomly throughout the polymer and wherein the R in $(OR)_n$ also may be composed of different aliphatic or aromatic hydrocarbon groups/blocks.

The length of the chain of each individual R in the repeating unit, $(OR)_n$, may be any number of carbon atoms, so long as the resulting polymer is essentially water insoluble, preferably having from 1 to about 30 carbon atoms, most preferably from 1 to about 15 carbon atoms. Additionally, cycloaliphatic and aromatic moieties may be appended to the aliphatics.

The terms "hydrocarbon", "aliphatic" (linear, branched and cyclo-) and "aromatic" as used herein are also intended to be inclusive of such groups containing one or more non-interfering substituent groups replacing hydrogen on the chains or rings of the hydrocarbon units (i.e., substituted hydrocarbon groups). As used herein, the term "non-interfering substituent (group)" means a substituent (group) that is essentially inert; i.e., does not interfere with the process of the present invention, i.e., the course of the depolymerization reaction and such substituent groups may readily be selected by those skilled in the art.

Although ordinary tap water may be used in the process, it is preferred to use distilled or deionized water substantially free of dissolved salts and particularly preferred to use water which has been

- 4 -

deoxygenated and is substantially free of dissolved oxygen. Removal of oxygen tends to minimize the occurrence of free radical side reactions during the process.

The amount of water used in forming the mixture with these polymers should be at least equal parts of water and polymer, but preferably at least about a two-fold excess, more preferably about a five-fold excess by weight. In general, the higher the water content of the mixture, the greater the expected conversion and conversion rate of the polymer at any given process temperature within the disclosed temperature range.

Conversely, the higher the process temperature within that range, the less water would be required to give rise to higher conversion rates of the polymer. The preferred water content of the mixture ranges from about 1:1 to about 10:1 by weight water to weight of polymer with 2:1 to 5:1 parts by weight being the preferred.

The process is conducted by introducing the liquid water and the polymer into a reaction vessel, forming an aqueous mixture thereof and heating the mixture under autogeneous pressure and at a temperature within the range of from about 200°C to about 374°C, preferably from about 200°C to about 350°C for a period of time sufficient to depolymerize the polymer by cleaving ether linkages in the polymer backbone. The reaction should be carried out preferably in an inert atmosphere, such as argon or nitrogen, as an aid in excluding oxygen from the system. The polymer may be introduced into the reactor in any form that can suitably be accommodated therein, for example as a powder, small chips or pieces cut to appropriate size.

The term "autogeneous pressure of the system" refers to the combined vapor pressure exerted by the mixed components present in the aqueous system heated at a particular process temperature. The autogeneous pressure of water alone in such a system ranges from about 225 psig to about 3200 psig over a temperature range of from about 200°C up to about 374°C the critical temperature of water. The autogeneous pressure of a system containing both water and the polymer

- 5 -

would be higher over this temperature range as a function of the polymer content and the partial pressure exerted by the polymer decomposition products.

The starting materials required in the process of the present invention are liquid water, preferably water having a pH of from about 7 to about 3.5, more preferably neutral water (pH equal to about 7.0) at room temperature, and a polymer containing repeating or multiple ether linkages in the backbone and otherwise having the characteristics described above. Thus, the process of the present invention may be further modified by adjusting the pH of the liquid water within the disclosed range to influence selectivity toward particular end products, depending on the pH of the water and the identity, strength and concentration of the materials used to produce the pH thereof. For example, the presence of small quantities of a stronger or weaker acid, may assist in obtaining higher rates of conversion of the polymer. The presence of stronger acids such as sulfuric, hydrochloric or phosphoric acid in the liquid water at levels of less than about 0.5 wt% is expected to produce higher polymer conversion rates but tends to disfavor selectivity towards the yield of alcohols and favor selectivity towards the production of olefins or other byproducts. The presence of weaker acids, such as acetic acid in the liquid water at levels of less than about 3 wt% is expected to produce higher polymer depolymerization rates but with greater selectivity toward the production of alcohols.

The terms "conversion", "degrading" and "depolymerization" as used herein are defined as cleavage of one or more C-O bonds in the ether linkages of the polymer backbone to produce more desirable, value added, lower molecular weight compounds than the starting polymer (i.e., alcohols, monomeric products and lower molecular weight oligomeric products). Some of these lower molecular weight compounds may be water soluble. Where the starting polymer ranges from about 5,000 to over 100,000 in average molecular weight, the product of the reaction may generally comprise a mixture composed primarily of the corresponding alcohol and oligomeric units containing preferably from about 1 to about 15 ether units as the major components. Depending on

- 6 -

the length of time that the reaction is carried out, it can effect the cleavage of the resulting oligomers (lower molecular weight compounds), if desired.

The process can be used to convert any weight percent of the starting polymer. Generally the percentage of conversion of polymer which may be achieved in accordance with the process of this invention may range from at least about 75% to quantitative amounts depending upon the number of ether linkages in starting polymer and reaction conditions. Reaction times of 0.1 hour to 8 hours are generally acceptable depending on the amount of water present, the temperature and the amount of conversion desired.

The process of the present invention may be particularly adapted for use in conjunction with other chemical processes wherein polymers with multiple or repeating ether linkages in the backbone are formed as a less valuable byproduct. The advantageous use of the present process in conjunction with other chemical processes where polymers having ether linkages in the backbone are formed as by-products should be evident to the skilled practitioner.

The process of this invention may be carried out in a batch or in a continuous mode using conventional pressure equipment. Examples of such equipment include a laboratory bomb, a high pressure autoclave, a stirred tank reactor or a continuous flow-through tube, each equipped with a heating means capable of achieving and maintaining the required temperatures and pressures over the required time period.

The invention may suitably comprise, consist or consist essentially of the elements thereof disclosed herein and may be practiced in the absence of any element not specifically disclosed.

- 7 -

EXAMPLESExample 1

Polyethylene glycol (1.0 g) (MW 100,000), in a solid, insoluble form, was mixed with H₂O (10.0 g) and heated at 350°C for 2 hours to produce a yellow solution (indicating that depolymerization of the insoluble starting material to lower molecular weight products had occurred).

Example 2

Polyethylene glycol (1.0 g) (MW 19,000), in a solid, insoluble form, was mixed with H₂O (10.0 g) and heated at 315°C for 1 hour to produce a colorless solution (indicating that depolymerization of the starting material to lower molecular weight products had occurred).

Example 3

Polyethylene glycol (1.0 g) (MW 100,000), in a solid, insoluble form, was mixed with H₂O (10.0 g) and heated at 315°C to produce a white, cloudy solution. GC, mass spec analysis showed alcohol and ether units in range of 1-13 units (indicating that depolymerization of the starting material to lower molecular weight products had occurred).

- 8 -

CLAIMS:

1. A process for depolymerizing high molecular weight polymers having ether linkages in the backbone, comprising:

(a) forming an aqueous mixture of liquid water and a polymer having multiple ether linkages in the backbone and a molecular weight of at least about 5,000; and

(b) heating said mixture to a temperature within the range of from about 200°C up to about the critical temperature of water under autogeneous pressure of the system for a period of time sufficient to depolymerize said polymer into lower molecular weight compounds.

2. The process of claim 1 wherein said polymer has the formula:



wherein the polymer has a molecular weight of at least about 5,000 and wherein R, R' and R'' may be the same or different and each is selected from the group consisting of unsubstituted aliphatic and aromatic hydrocarbon groups and substituted aliphatic and aromatic hydrocarbon groups, wherein at least one of R, R' and R'' is not an unsubstituted phenyl group, and wherein n is a whole number of at least about 100.

3. The process of claim 1 wherein said aqueous mixture contains from about 1:1 to about 10:1 parts by weight of water per part by weight of polymer.

4. The process of claim 1 wherein said mixture is heated at a temperature of from about 200°C to about 350°C.

- 9 -

5. The process of claim 1 wherein said aqueous mixture contains from about 2:1 to about 5:1 parts by weight of water per part by weight of polymer.

6. The process of claim 1 wherein the liquid water has a pH of about 7.0.

7. The process of claim 1 wherein the liquid water has a pH of from about 7 to about 3.5.

8. The process of claim 2 wherein the polymer is polyethylene glycol.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US93/01850**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(S) : C07C 41/01

US CL : 568/606,609,617,618,619,620

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 568/606,609,617,618,619,620

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A, 4,806,658 (Chang et al.) 21 February 1989 see entire document.	1-8
Y	US,A, 5,043,486 (Sisken et al.) 27 August 1989 see entire document.	1-8
Y	US,A, 4,581,470 (Hoy et al.) 08 April 1986 see entire document.	1-8

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be part of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed		"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family
---	--	--

Date of the actual completion of the international search

04 MAY 1993

Date of mailing of the international search report

07 JUN 1993

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

HOWARD T. MARS

Telephone No. (703) 308-1235

 Ngwenke Ngwenke
 EGUEZI NGOC-HO
 INTERNATIONAL DIVISION